

Imaging Structures and Measuring Forces at Nanoscales with Atomic Force Microscopy

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Zobrazovanie štruktúr a meranie síl na nanometrickej úrovni atómovou silovou mikroskópiou

Interaction between interfaces in solution of chemical reagents is scientifically and technologically significant. Atomic force microscopy has been used to visualise structures of adsorbed surfactant molecules and measure interaction forces between surfaces with adsorbed molecules. This paper presents the results obtained by the author and associates in three major research strands, including imaging structures of surfactants adsorbed at solid-liquid interfaces, measuring interfacial forces between water-repellent (hydrophobic) surfaces and microhydrodynamic forces between an AFM colloid probe and a soft interface. The research increases our understanding of the role of surfactants and interaction forces in particle technology and interface science.

Key words: self-assembled surface structures, interfacial forces, atomic force microscopy.

Introduction

The atomic force microscope (AFM) was invented in 1986 by the Nobel-prize award winner, Dr. G. Binnig (Binnig, 1986), and has been used for imaging nanostructures and measuring atomic and molecular forces with conducting and non-conducting surfaces in many fields of nanoscience and nanotechnology. AFM can provide the ability to view and understand events as they occur at the molecular level which will increase our understanding of how systems work and lead to new discoveries in many fields, including materials science, electrochemistry, polymer science, biophysics, life science, and nanobiotechnology.

In colloid and interface science and technology, AFM has been used to image surfaces with adsorbed surface-active agents (surfactants) with nanoscale resolution as well as measure extremely small surface and molecular forces ($\sim 10^{-12}$ N) in the gas and liquid phases. This paper presents some selected outcomes of the author research in three major research strands, including:

- 1. Structures of self-assembled surface micelles of surfactants adsorbed at solid-liquid interfaces:** Surfactant adsorption at solid-liquid surfaces is of significant importance in many particulate processes ranging from particle separation and enhanced oil recovery to pharmaceuticals, paint technology, high quality ceramics production, and mineral processing (Shah, 1998). Stability of the dispersions is related not only to the amount of adsorbed surfactant but also to the structure of the adsorbed surfactant molecules at the interface. The structures depend on the type of surfactants and the properties of the water-solid interfaces. Different types of micellar structures have been observed at the surfaces for surfactant concentrations around the critical micelle concentration (CMC).
- 2. Role of dissolved gas on attraction between hydrophobic surfaces:** This attraction, known as the hydrophobic force, is critically important for interaction and attachment of hydrophobic particles in coal and mineral flotation (Skvarla, 2001), oil droplets in pharmaceutical formulas and biological cells (Israelachvili, 1992). However, the origins and models for this attractive force between hydrophobic surfaces have been a source of debate since the first direct measurements of this force in the early 1980's (Christenson and Claesson, 2001). Attraction between an AFM hydrophobic probe and a flat hydrophobic surface has been studied in water, in water-ethanol mixtures, and in water saturated by gases with different solubilities. Experimental results indicate the role of surface stabilized submicron-sized bubbles in the hydrophobic attraction.
- 3. Microhydrodynamic interaction between a solid particle and a soft interface:** Interaction between a solid particle and a soft interface such as an air bubble or an oil drop is a key to understanding emulsification and particle separation using air bubbles (Nguyen and Schulze, 2004). The AFM colloid probe technique has been used to measure hydrodynamic interaction forces between a solid sphere and an air bubble, as well as intermolecular and surface forces.

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Materials and Methods

Surface images of surfactants and forces between a spherical particle and a flat surface were determined with the Nanoscope IIIa and PicoForce AFM's (Digital Instruments/Veeco, USA). The interaction force between a surface and a particle was measured using the AFM colloid probe technique (Butt, 1991; Ducker et al., 1991). The micron-sized sphere was attached to the end of an AFM microfabricated cantilever. The flat surface was mounted to a piezoelectric transducer and was moved relatively to the particle at constant speeds. The cantilever deflection due to the surface-particle interaction was measured with a laser beam reflected from the cantilever onto a split photodiode. The force measurements with soft surface such as an air bubble or an oil drop attached to the piezoelectric transducer were carried out using the same technique.

The surface interaction forces were determined by multiplying the cantilever deflection by the spring constant. The cantilever deflection was determined from the voltage signal of the photodiode employing a scaling procedure, which used the linear displacements between the cantilever and the surface. The separation was then determined from the cantilever deflection and the displacement of the piezoelectric transducer.

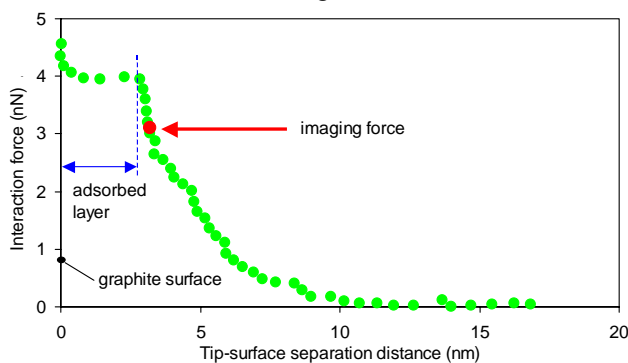
Imaging self-assembled surfactant structures at water-solid interfaces was carried out using the soft-contact technique (Manne et al., 1994; Manne and Gaub, 1995). The technique used a microfabricated cantilever with a shape tip (~ 10 nm radius) to probe a force, which was just delicate enough to distinguish surfactant surface structures without actually disturbing them. The force was then maintained constant during the tip scanning over the surface. The change in position of the tip for maintaining the constant force produced images of the adsorbed structures at the solid surface.

Silicon nitride cantilevers (Digital Instruments/Veeco, USA) with nominal spring constant of 0.12 N/m were used. The particles and surfaces used in the experiments included glass and silica micro-spheres, silicon wafers, microscope glass slides, highly ordered pyrolytic graphite (HOPG), fused alumina surface, and mica. The silica and glass surfaces were made hydrophobic by a silanation process. The contact angle measured with a sessile drop apparatus was 62 degrees for the silanated surfaces.

The chemicals used in the experiments included two surfactants (sodium dodecyl sulphate, SDS, and cetyl trimethyl ammonium bromide, CTAB) and NaCl for controlling the electrical double-layer interaction between the surfaces. Deionized water from a Millipore Milli-Q system was used in cleaning glassware and the apparatus, and in preparing all solutions. All the chemicals used were of analytical grade. For the measurements with dissolved gases, water was first outgassed by subsequent boiling/freezing under low pressure several times and was then saturated by the required gas directly in the AFM liquid cell.

Results and Discussion

Fig. 1 shows a typical force curve for a silicon nitride cantilever approaching a surface in a solution of 0,4 mM SDS and 0,1 M NaCl. A force of ~ 3 nN was used to image the adsorbed monolayer of SDS on the graphite surface. The images of SDS adsorbed at hydrophobic graphite surfaces show linear, parallel aggregates oriented perpendicular to a symmetry axis and spaced apart by a little over twice the surfactant length (Fig. 2A). These observations are consistent with half-cylindrical aggregates wherein molecules adjacent to the surface are arranged tail to tail along parallel strips, with the hydrophobic alkyl chains oriented parallel to a graphite symmetry axis. At the hydrophilic, negatively charged, mica surface wormy micelles were observed. These structures are consistent with a cylindrical structure where the surfactant molecules first adsorb through the electrostatic interaction between the oppositely charged head group



and the mica surface (Fig. 2D). On amorphous mineral oxide surfaces, such as alumina and silica, spherical structures have been observed (Fig. 2B & 2C). Clearly, the surface charge of these surface micelles plays an important role in their formation and is crucial for the modelling of this self-assembly process involving the formation of surface micellar structures (Paruchuri et al., 2004).

Fig. 1. Typical force curve for a cantilever (with a 10 nm radius tip) approaching a HOPG graphite surface in a solution of 0.4 mM SDS and 0.1 M NaCl.

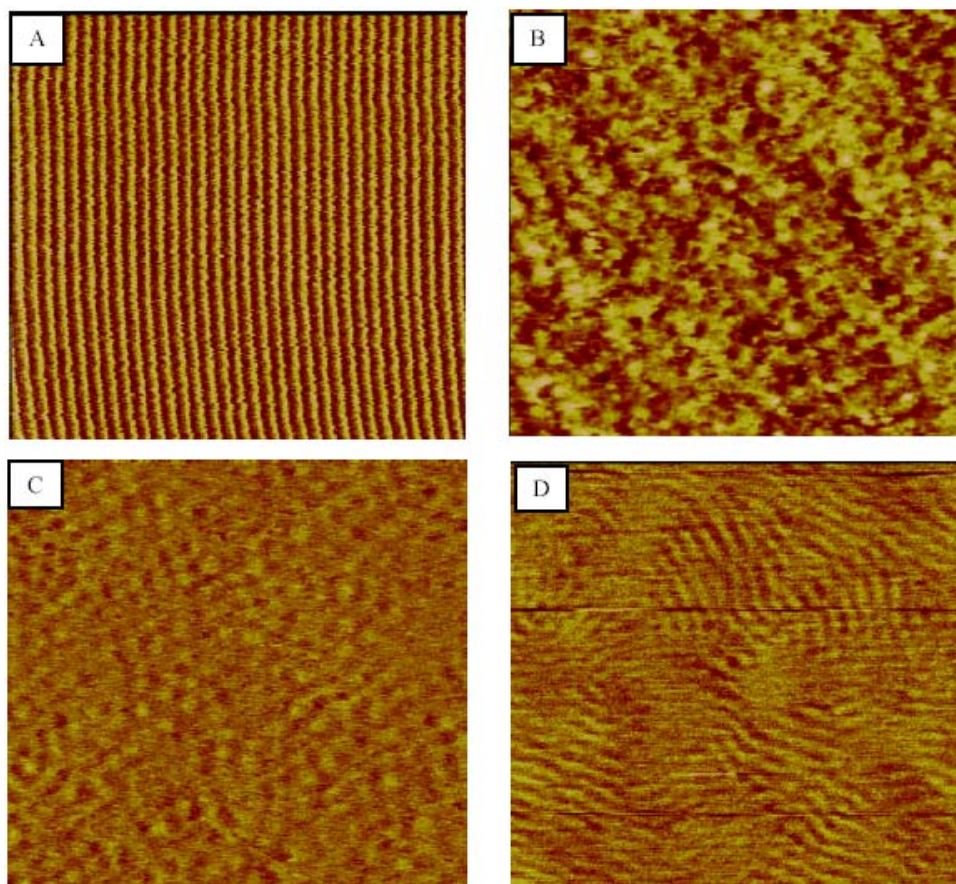


Fig. 2. Images ($200 \text{ nm} \times 200 \text{ nm}$) of surface surfactant structures obtained by the soft contact AFM technique. A. Hemi-cylindrical structures of SDS at a hydrophobic graphite surface. B. & C. Spherical structures of SDS at a positively charged fused alumina surface and of CTAB at a negatively charged silica surface. D. Short worm-like cylindrical structures of CTAB at a hydrophilic negatively charged mica surface (Paruchuri et al., 2004).

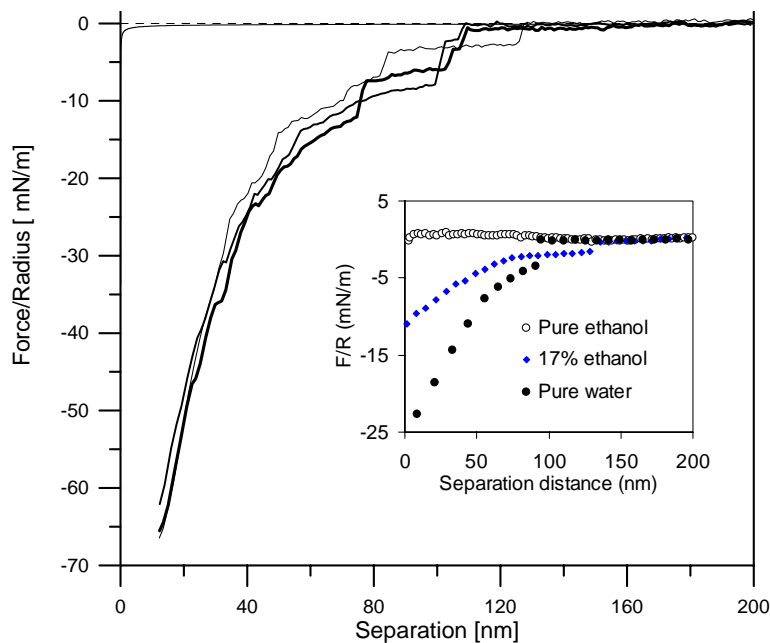


Fig. 3. AFM results obtained for the scaled force, F/R , between hydrophobic glass spheres (radius $R = 4 \mu\text{m}$) and plates in water saturated with argon and in ethanol-water mixtures (Nguyen et al., 2003b).

Effect of ethanol and argon dissolved in water on the force between hydrophobic (silanated glass) surfaces is shown in Fig. 3. The steps in the force curves are due to the formation of bridging gas micro-bubbles between hydrophobic surfaces (Attard, 1996; Attard et al., 2002). The addition of ethanol to water increases the jump-in distance, where the step in the force curve occurs and decreases the strength of the measured force, to the extent that for mixtures with a high content of ethanol the step is difficult

to measure. Ethanol decreases the liquid-vapour surface tension, leading to the decrease in the attractive force. The influence of gas solubility on the hydrophobic attraction has been investigated with different gases, including argon (solubility in water 34,2 mL/L), nitrogen (solubility in water 15,8 mL/L), and helium (solubility in water 8,6 mL/L). Solubility of gases in ethanol is also higher than in water. The size of the observed steps on the force curves depends on the solubility of the gas used to saturate water: The higher the solubility, the larger the size of the steps. However, the strength and the range of the attractive force in the water saturated by the gases appear to be the same, indicating that the gas solubility is not a controlling factor. It is important to note that surface roughness and heterogeneities due to crystallites and patchy of the adsorbed surfactants can control the formation and stability of submicroscopic gas bubbles at the solid-liquid interface.

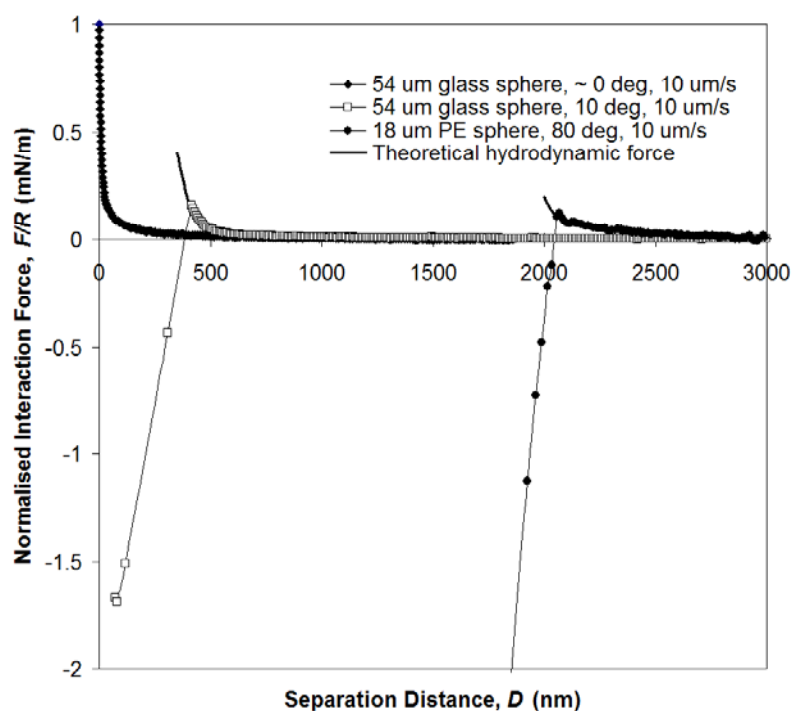


Fig. 4. Scaled force, F/R , between air bubbles ($R \approx 250 \mu\text{m}$) in deionized water and spherical particles with different hydrophobicities (contact angles). The approach speed between the surfaces was $10 \mu\text{m/s}$ (Nguyen et al., 2003a).

Typical results for the interaction force with soft interfaces are shown in Fig. 4. The interaction forces are indeed of very long range, in particular, at high approach speeds. This long range indicates that the hydrodynamic interaction is significant at high approach speeds between a bubble and a particle in flotation. The microhydrodynamic resistance force due to the intervening water film between the surfaces increases with decreasing separation distance (film thickness) as predicted (Nguyen and Evans, 2002). Due to strong attraction between the hydrophobic surfaces, the intervening liquid films between the bubble and the hydrophobic particles are not stable, and the rupture of the intervening water film and the attachment of the particle to the air bubble take place. For the data shown in Fig. 4 for the polyethylene (PE) particle, which was of a greater degree of hydrophobicity (the contact angle was about 80 degrees), the jump-in-contact interaction and the contact force were extremely strong and the force curves were not fully captured in the 'force window' of the AFM system. Our force measurements also show that the jump-in separation distances increase with approach speeds which supports the existence of submicroscopic bubbles on hydrophobic surfaces, as shown by the steps in Fig. 3 as well as by direct AFM images (Ishida et al., 2000; Tyrrell and Attard, 2002; Steitz et al., 2003). The bubbles become very unstable at high approach speeds and cause the attraction at large separation distances. This feature can complicate the analysis of the interaction force at high approach speeds and separation distances. Further systematic investigations of the bubble-particle interaction under the influence of both attractive surface and repulsive hydrodynamic forces are in progress.

In the case of the hydrophilic sphere (with contact angle of $\sim 0^\circ$) shown in Fig. 4, the rupture of the intervening water film and the attachment of the particle to the air bubble did not take place. At short distances, significant deviations of strong repulsive force between hydrophilic spheres from the model prediction are related with the deformation of air-water interface due to the particle approach, as well as intermolecular and surface forces.

Conclusion

Atomic force microscopy has been used to image structures of surfactants adsorbed at solid surfaces in water and measure interaction forces between the surfaces. Depending on the type of surfactants and the surface, different types of micellar arrangements at the surfaces have been observed. Dissolved gases have an important effect on attraction between hydrophobic surfaces in liquids. Microhydrodynamic interactions between a solid particle and a soft interface have been determined for both hydrophobic and hydrophilic solid surfaces.

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